Pinning and switching of magnetic moments in bilayer graphene

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Abstract. We examine the magnetic properties of the localized states induced by lattice vacancies in bilayer graphene with an unrestricted Hartree-Fock calculation. We show that with realistic values of the parameters and for experimentally accessible gate voltages we can have a magnetic switching between an unpolarized and a fully polarized system.

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1. Introduction

After the explosion of publications on graphene following the experimental synthesis [1, 2] the present attention is centered on the experimental advances aiming to generate better samples for electronic devices. One of the major problems preventing applications of single layer graphene (SLG) is the difficulty to open and control a gap in the samples. To this respect bilayer graphene (BLG) and multilayer samples are more promising [3]. One of the potentially most interesting aspects of graphene for the applications and that remains up to now partially unexplored concerns the magnetic properties. Ferromagnetic order enhanced by proton irradiation has been observed in graphite samples [4] and demonstrated to be due to the carbon atoms by dichroism experiments [5]. By now it is clear that the underlying mechanism leading to ferromagnetism in these carbon structures is the existence of unpaired spins at defects induced by a change in the coordination of the carbon atoms (vacancies, edges or related defects) [6]. Very recent experiments on thin films in irradiated graphite show that the main effect of proton irradiation is to produce vacancies on the outer layers of the samples. For thin enough films of a few thousands angstroms the protons go through the samples leaving some vacancies behind. These samples show an enhanced local ferromagnetism and also a better conductivity than the untreated samples with less defects [7]. Vacancies can play a major role on these magnetic and transport properties and are lately been recognized as one of the most important scattering centers in SLG and BLG [8].

The existence and nature of localized states arising from vacancies in BLG have been analyzed in a recent paper [9]. It was found that the two different types of vacancies that can be present in the BLG system – depending on the sublattice they belong to – give rise to two different types of states: quasi-localized states, decaying as $1/r$ for $r \to \infty$, similar to these found in the SLG case [10], and truly delocalized states, going to a constant as $r \to \infty$. When a gap is induced by the electric field effect quasi-localized states give rise to resonances at the gap edges while the delocalized ones become truly localized inside the gap. These findings are very important in understanding the magnetic properties of the graphitic samples since these localized states carry magnetic moments. In this paper we study the magnetic properties of the localized states found in [9] using an unrestricted Hartree-Fock calculation. The most interesting case arises in the presence of a gate (perpendicular electric field $\mathbf{E} = E_z\,\hat{e}_z$) opening a gap when considering two vacancies of the same sublattice located at different layers. We will show that with realistic values of the parameters and for experimentally accessible gate voltages we can have a magnetic switching between unpolarized and fully polarized system.

2. The electronic structure of bilayer graphene

The lattice structure of a BLG is shown in figure 1. In this work we consider only AB-Bernal stacking, where the top layer has its A sublattice on top of sublattice B of the bottom layer. We use indices 1 and 2 to label the top and bottom layer, respectively.

In the tight-binding approximation, the in-plane hopping energy, t, and the inter-layer hopping energy, γ_1, define the most relevant energy scales (see figure 1). The simplest tight-binging Hamiltonian describing non-interacting $\pi-$electrons in BLG reads [11, 12, 13]:

$$H_{TB} = \sum_{i=1}^{2} H_i + \gamma_1 \sum_{\mathbf{R},\sigma} \left[a^{\dagger}_{1,\sigma}(\mathbf{R}) b_{2,\sigma}(\mathbf{R}) + \text{h.c.} \right], \tag{1}$$

with H_i being the SLG Hamiltonian

$$H_i = -t \sum_{\mathbf{R},\sigma} \left[a^{\dagger}_{i,\sigma}(\mathbf{R}) b_{i,\sigma}(\mathbf{R}) + a^{\dagger}_{i,\sigma}(\mathbf{R}) b_{i,\sigma}(\mathbf{R}-\mathbf{a}_1) + a^{\dagger}_{i,\sigma}(\mathbf{R}) b_{i,\sigma}(\mathbf{R}-\mathbf{a}_2) + \text{h.c} \right], \tag{2}$$

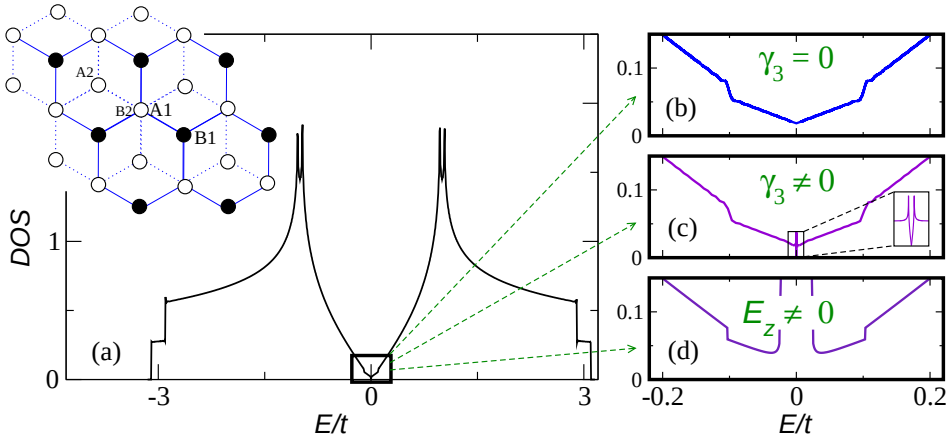

Figure 1. (a) Total DOS of bilayer graphene. The inset shows the lattice structure. (b)-(d) DOS zoom at low energies for the minimal model, for the model with γ_3, and the model with finite gap due to perpendicular electric field E_z, respectively.

where $a_{i,\sigma}(\mathbf{R})$ $[b_{i,\sigma}(\mathbf{R})]$ is the annihilation operator for electrons at position $\mathbf{R}$ in sublattice Ai (Bi), $i = 1, 2$, and spin σ. The basis vectors may be written as $\mathbf{a}_1 = a\,\hat{\mathrm{e}}_\mathrm{x}$ and $\mathbf{a}_2 = a(\hat{\mathrm{e}}_\mathrm{x} - \sqrt{3}\,\hat{\mathrm{e}}_\mathrm{y})/2$, where $a = 0.246\,\mathrm{nm}$. The estimated values of the parameters for this minimal model are: $t \approx 3\,\mathrm{eV}$, $\gamma_1 \approx 0.3\,\mathrm{eV} \sim t/10$ [14].

The main additional tight binding parameters are the inter-layer second-nearest-neighbor hoppings γ_3 and γ_4 shown in figure 1 which play an important role in what follows. γ_3 connects different sublattices $(B1 - A2)$ and γ_4 connects atoms of the same sublattices $(A1 - A2$ and $B1 - B2)$. Their values are less well known but we can assume that the following relation between parameters holds, $\gamma_4 \sim \gamma_3 \sim \gamma_1/3 \sim t/30$.

For the analysis of the bound states and associated magnetic moments of the present work a summary of the most relevant issues of the BLG electronic structure is the following:

- The minimal model with only γ_1 has electron-hole symmetry and it is a bipartite lattice although not all the A and B atoms are equivalent since some have (have not) a hopping to the other layer. It has two degenerate stable Fermi points similar to SLG [15] but the dispersion relation around them is quadratic and the density of states (DOS) at the Fermi points is finite (figure 1(b)). Opening of a gap gives rise to the DOS shown in figure 1(d) with the characteristic double minimum shape [16]. The value of γ_1 sets a bound on the maximal value of the gap.
- Inclusion of a γ_3 together with γ_1 coupling lifts the degeneracy of the Fermi points that are shifted in momentum space. The dispersion relation around the Fermi points is linear and the DOS is zero very much like in the SLG case (figure 1(c)). The lattice is still bipartite in the sense that, generically, atoms of type A are only linked to atoms of type B although the layer index and couplings make some differences between different A (B) atoms.
- The combination γ_1-γ_4 breaks the bipartite nature of the lattice. On the electronic point of view it induces an electron-hole asymmetry but the DOS at the Fermi point does not change. This coupling is important for the magnetism of the samples.

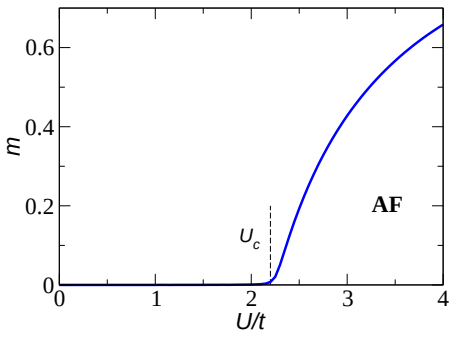

Figure 2. Sublattice magnetization $m = |n_{\Gamma i,\uparrow} - n_{\Gamma i,\downarrow}|$ vs U for bilayer graphene in the Hartree-Fock approximation, where $\gamma_1 = 0.1t$ and $\Gamma i = A1, B1, A2, B2$.

3. The model and the magnetic properties of the perfect lattice

In order to study the magnetic behaviour of BLG in the presence of vacancies and/or topological defects we use the Hubbard model, treated in the Hartree-Fock approximation. The total Hamiltonian then reads $H = H_{TB} + H_U$, where the on-site Coulomb part is given by

$$H_U = U \sum_{\boldsymbol{R},\iota} [n_{a\iota\uparrow}(\boldsymbol{R}) n_{a1\iota\downarrow}(\boldsymbol{R}) + n_{b\iota\uparrow}(\boldsymbol{R}) n_{b\iota\downarrow}(\boldsymbol{R})] \,, \tag{3}$$

where $n_{x\iota\sigma}(\boldsymbol{R}) = x^{\dagger}_{\iota\sigma}(\boldsymbol{R}) x_{\iota\sigma}(\boldsymbol{R})$, with $x = a, b$, $\iota = 1, 2$ and $\sigma = \uparrow, \downarrow$. We use finite clusters with periodic boundary conditions at half-filling (one electron per atom).

It is well known that the Hartree-Fock-RPA approximation for SLG produces a phase transition at the critical Hubbard interaction $U_c \approx 2.2t$, above which the staggered magnetization becomes finite [17, 18].

The antiferromagnetic transition in the BLG case has been analyzed in [19]. Figure 2 shows the sublattice magnetization as a function of the Hubbard repulsion U. Throughout this work we will explore the magnetic behaviour of the system with vacancies for values of $U \leq t$ deep into the region of U where the sublattice magnetization is exponentially suppressed so that we can attribute any magnetic moment to the presence of defects.

4. Vacancies in bilayer graphene

Unlike the case of clean undoped SLG where the DOS at the Fermi level is zero and there is no gap, in the BLG case and depending on the more relevant tight binding parameters (see figure 1) we can have either a constant DOS – minimal model with only t and γ_0 – or a zero DOS in the presence of γ_3. Moreover a gap can be easily generated by an electric field perpendicular to the plane, as mentioned before. The DOS is crucial for the study of localized states. In the SLG case, single vacancies induce quasi-localized states around the defect, decaying as $1/r$ [10, 20]. Due to the absence of a gap, true bound states do not exist in the thermodynamic limit.

In the BLG case there are two types of vacancies *beta* and *alpha* for sites connected (or not) to the other layer. As shown in [9] associated to the presence of vacancies and to the existence of a gap in the spectrum generated by an electric field E_z three different types of vacancy-induced states are found:

(i) For $E_z = 0$ a $\beta-$vacancy induces a resonance for $\gamma_3 = 0$ (delocalized state) and a quasi-localized state ($1/r$ behaviour) for a finite value of γ_3.

(ii) For $E_z = 0$ an $\alpha-$vacancy induces always a resonance irrespective of γ_3.

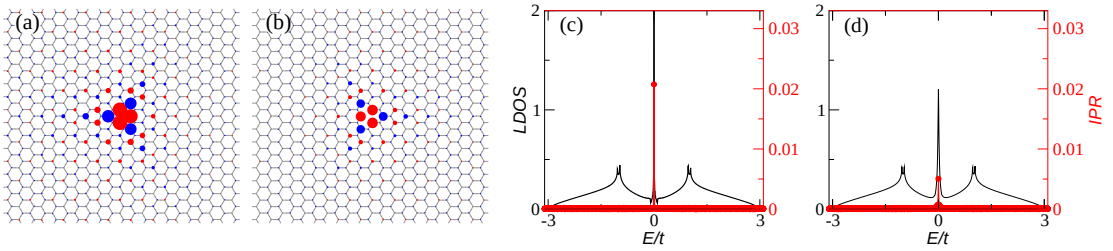

Figure 3. (a)-(b) Zero-energy eigenstates in a minimal model bilayer graphene cluster with $\gamma_1 = 0.1t$ containing a single $\beta-$ (a) and $\alpha-$vacancy (b). We show only the region around the vacancy and the layer where the vacancy is located. (c)-(d) Local density of states (right axis) and inverse partition ratio (left axis) for a cluster with a single $\beta-$ (c) and $\alpha-$vacancy (d) including $\gamma_3 = 0.033t$.

(iii) For $E_z \neq 0$ a $\beta-$vacancy produces a resonance inside the continuum near the band edge while an $\alpha-$vacancy gives rise to a truly localized state inside the gap. This is the most interesting state for the magnetic implications.

In figure 3(a) and 3(b) we illustrate the nature of the localized states by plotting the numerical wavefunction for zero-energy eigenstates in a BLG cluster with a single $\beta-$ and $\alpha-$vacancy, respectively. The cluster contains 2×74^2 sites. The image shows only the layer where the vacancies are located and the region around the vacancies. It can be seen that a quasi-localized state exists for a $\beta-$vacancy, and for an $\alpha-$vacancy the zero-energy mode also appears quasi-localized over the diluted layer. The reduced amplitude of the zero mode in figure 3(b) for the $\alpha-$vacancy is due to the presence of a delocalized component on the underlaying layer (not shown).

The above results are confirmed by the enhanced local DOS and enhanced inverse partition ratio at zero energy for a $\beta-$vacancy (quasi-localized state), as shown in figure 3(c). The equivalent result for a $\alpha-$vacancy (delocalized state with a quasi-localized component in one of the layers) is shown in figure 3(d). The local DOS is computed at a site closest to the vacancy using the recursive Green's function method for a cluster with 2×1400^2 sites. The inverse participation ratio, defined as fourth moment of the wavefunction amplitude, is computed for the cluster used in figures 3(a) and 3(b).

5. Magnetic behaviour

The generation and structure of the magnetic moments associated to unpaired atoms in SLG and multilayer graphene is to a great extent determined by the bipartite nature of the underlying lattice and hence by the Lieb's theorem [21]. The theorem states that the ground state of the repulsive half filled Hubbard model in any bipartite lattice with $N = N_A + N_B$ sites is unique and has total spin $S = \frac{1}{2}|N_A - N_B|$. According to the Lieb's theorem [21] the quasi-localized zero modes induced by unpaired atoms in the bipartite lattice become spin-polarized in the presence of a Hubbard repulsion U and local moments appear in the lattice [20, 22, 23, 24, 25]. In the thermodynamic limit the spin polarized modes (no longer at zero energy) merge into the continuum and even though Lieb theorem applies equally, the spin polarization is delocalized and itinerant ferromagnetism appears [21].

Pinning of magnetic moments in localized regions, in the thermodynamic limit, would be a very interesting possibility for applications. In SLG we could try to open a gap and push the quasi-localized modes out of the continuum. However, a gap is not easily open in graphene, and

a mass-gap does not work: the same linear algebra theorem that guarantees the existence of zero modes when no diagonal terms exist in the Hamiltonian [26] also states that, in the presence of a staggered (diagonal) potential, these modes move to the gap edges; this is due to the fact that these modes live only on one sublattice, the less diluted. In BLG we can easily open a gap by inducing layer asymmetry through the application of a perpendicular electric field $E_z \neq 0$ (back gate, for example), which is not a staggered potential. In [9] it was proven that truly localized states exist inside the gap induced through electric field effect in BLG.

5.1. Single vacancy

The magnetic properties of a vacancy in BLG were studied in [27] using spin-polarized density functional theory. It was found that the spin magnetic moment localized at the vacancy is of the order of ten percent smaller than that of SLG for both types of vacancies α and β. This reduction of the spin magnetic moment in the bilayer was attributed to the interlayer charge transfer from the adjacent layer to the layer with the vacancy. We have verified that both in the minimal model $\gamma_3 = 0$ and for a finite value of γ_3 we obtain the results expected for a single layer in accordance with Lieb theorem. The second-nearest-neighbor hopping γ_4 that breaks the bipartite character of the whole lattice does not change this behaviour, as long as one vacancy is considered. A finite γ_4 makes the vacancy-induced state to appear off zero energy, but still spin degenerate. Including U lifts spin degeneracy and induces a magnetic ground state. The situation is similar to the one discussed in SLG [25] when a pentagon is included.

5.2. Two vacancies and the effect of an asymmetry gap

Regarding the effect of two vacancies, we have found rather different behaviour depending on whether an asymmetry gap is present or not, and depending on the combination layer/sublattice where the two vacancies occur. As mentioned before, such an asymmetry gap is induced by making the two layers asymmetric, for example, by applying a perpendicular electric field through a back gate voltage. The resultant electrostatic energy difference between layers eE_zd ($d = 0.34\,\mathrm{nm}$ is the interlayer distance and e the electron charge) introduces an interesting tuning capability to the system since all other parameters, including the strength of the Hubbard interaction U, can hardly be tuned in experiments.

For the bipartite case where $\gamma_4 = 0$ results are in complete agreement with Lieb theorem, as expected. In particular, irrespective of the layer index, two vacancies of the same sublattice induce a total spin $S = 1$, while vacancies in different sublattices give rise to a ground state with $S = 0$. When $E_z \neq 0$, since there are nonzero diagonal elements in the Hamiltonian matrix, we no longer have a bipartite system in the Lieb sense [21] and different behaviour from these determined by Lieb theorem might arise. We have found that two vacancies in different sublattices always give $S = 0$, irrespective of the layer index and of the gap's size, in accordance with Lieb theorem. Also following Lieb, vacancies in the same sublattice, and belonging to the same layer, i.e. Ai, Ai or Bi, Bi with $i = 1, 2$, originate $S = 1$.

The interesting case arises when the system is gaped and has two vacancies from the same sublattice in different layers, i.e. $A1, A2$ or $B1, B2$. In this case we have two regimes: for small E_z we get $S = 1$ in agreement with Lieb theorem. When E_z increases we reach a regime at a critical value of E_z where the ground state has $S = 0$. Inclusion of the γ_4 hoping goes in the same direction as the gap depressing the polarization. The critical U to maintain the full polarization of the lattice increases for bigger values of γ_4. The critical line in the $E_z - U$ plane is shown in figure 4 for different values of γ_4. The explanation for this behaviour lies in the different ways in which the degeneracy of the zero modes is lifted with U – that splits the degeneracy according to the spin – and with other couplings like E_z, γ_4, or in-plane next-nearest-neighbor t' [28]. It is

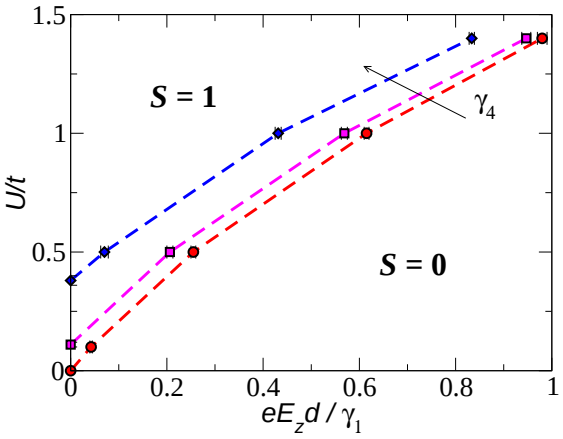

Figure 4. Transition line between total spin $S = 1$ and $S = 0$ in the $E_z - U$ plane for the ground state of a bilayer system with two vacancies belonging to the same sublattice located in different layers for different values of the γ_4 hopping integral. Circles (blue) , squares (purple), and diamonds (red) stand for $\gamma_4 = 0, \gamma_1/4, \gamma_1$, respectively. The error bar is of the order of symbol size.

important to note that the transition between finite and zero magnetic polarization of the lattice occurs in the region of experimentally relevant values of the external voltage: $0 < E_z d \lesssim \gamma_1$ [29], which makes the realization and observation of such magnetic switching capability a real possibility.

6. Conclusions and discussion

We have examined the magnetic properties of the localized states induced by lattice vacancies in BLG recently analyzed in [9]. We have found that in the presence of a gap the system supports two types of spin polarized local states related to the two types of inequivalent vacancies that can exist in a Bernal stacking. Those living inside the gap are truly normalizable bound states what can give rise to fully localized large magnetic moments if there are several vacancies belonging to the same graphene layer. This can be related to the measurement of local magnetic moments in proton bombarded graphite associated to the defects [30] and to the observation of the insulating nature of the ferromagnetic regions [31]. A density of such vacancies would give rise to a mid-gap band contributing to the total conductivity of the sample. In such band many body effects will be important and can drive the system to other kinds of instabilities [32]. The other type of vacancies stay at the edge of the gap and give rise to quasi-localized magnetic moments whose wave function decays as $1/r$ similar to the states induced by vacancies in the monolayer systems.

The most interesting case arises in the presence of a gate opening a gap when considering two vacancies of the same sublattice located at different layers. We have shown that with realistic values of the parameters and for experimentally accessible gate voltages we can have a magnetic switching between unpolarized and fully polarized system.

Under the physical point of view our analysis can help to understand the local ferromagnetism measured in thin films of irradiated graphite [30] and the recent reports of an increasing of the conductivity of the thin films of graphite after irradiation with protons whose main effect is to produce vacancies on the samples [7].

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